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Supersonic Waves.

SUPERSONIC waves are sound waves of such high frequency that they are far beyond the limit of audibility. Their production depends on the inverse piezoelectric effect whereby a plate, asymmetrically cut from a quartz crystal, alternately contracts and expands when a periodically varying potential difference is applied to its opposite faces, with the production of elastic vibrations of high amplitude when resonance is obtained. The method of production of these waves was developed by Langevin in 1917 in connection with work on the detection of the presence of submarines by the echo of a narrow beam of high-frequency sound waves.

The waves have many surprising properties. If they arise vertically from a horizontal plate immersed in oil, they may exert a substantial upward thrust which will support a considerable weight at the surface of the oil, or they may project drops of oil 30 or 40 centimetres above the level of its surface. A mercury thermometer placed in the oil will register approximately the atmospheric temperature, but the thermometer appears hot to the touch on account of the friction between the vibrating stem and the fingers. Emulsions or fine dispersions can be obtained by passing supersonic waves across the boundary between oil and water or between mercury and water. The waves may be used for agglomerating suspended particles in liquids and in gases; by their means chemical reactions may be accelerated and crystallisation caused to begin.

These and other uses of supersonic waves are referred to in an article by E. Hiedemann in *Stahl und Eisen* (Vol. 56, May 21st, 1936, page 600). The main object of this article is to emphasise possible metallurgical developments in the use of high-frequency sound waves. Certain physical uses are well established. The waves have been used for measuring the depth of lakes by observing the time which elapses before an echo appears after the high-frequency signal has been directed downwards. They are also used for continuous sounding by ships at sea; but their metallurgical applications have, in general, not been developed.

It appears desirable that certain effects of magnetostriction and of high-frequency electrical oscillations (such effects, for example, as the acceleration of the nitriding process under the action of high-frequency alternating currents) should again be examined in the light of the possible influence of high-frequency mechanical vibrations. Supersonic waves are known to liberate gases from solutions, probably by the mechanical formation of minute cavities into which the gases diffuse, eventually giving rise to gas bubbles, and their use for de-gassing molten metals has been suggested.

Neither on this nor on the allied proposal of their use for promoting the separation of slag inclusions is there any actual record of successful experiments, but there is some evidence of the effect of the waves on grain size. Lately, S. Sokoloff has carried out experiments on the effect of supersonic waves on solidifying metals, and using a special form of wave emitter seems to have obtained evidence of a finer and more acicular structure in zinc which had solidified under the influence of supersonic waves than in the metal which had solidified under similar conditions, except that no waves were being passed through it.

The application on which most emphasis is laid by Hiedemann is the use of supersonic waves for the non-destructive testing of materials in the place of X-rays or γ-rays. In order to give a sound shadow in the path of ordinary sound waves an obstacle of large dimensions is required, but supersonic waves on account of their small wave length are scattered or reflected by relatively small objects. The permeability of iron and steel to supersonic waves is very great, but the presence in the material of fine cracks or cavities completely intercepts the progress of the waves at the position of the defect, or reduces the amount transmitted to a very small value. The first proposal to use supersonic waves for non-destructive testing was made by Mülhäuser in 1931. He employed a high-frequency sound emitter and detector, and by displacement of these over the opposite surfaces of a slab of metal was able to detect cavities, internal cracks, and surface flaws.

Later, the method of detecting the passage of the waves was greatly refined by Sokoloff, who made use of the fact, discovered by Debye and Sears, that a liquid traversed by supersonic vibrations behaves, in suitable conditions, like an optical diffraction grating. The regular compression and rarefaction of the medium act as the lines and spacings of the grating, and the distance between these compression "lines" is equal to the wave length of the supersonic waves. That the grating as a whole is moving with the velocity of sound is immaterial, since the velocity of sound is so small compared with the velocity of light. The intensity of the diffraction bands depends on the intensity of the supersonic vibrations transmitted through the steel.

In Sokoloff's experiments the end of the steel specimen under observation formed one wall of a container full of liquid (usually transformer oil) across which the waves, emerging from the steel, were transmitted. A beam of light was directed through the liquid, at right angles to the path of the waves and the interference fringe observed. When the steel was sound and homogeneous sharp diffraction bands were obtained; when it contained defects, the diffraction pattern was weakened and blurred. The work of Sokoloff on this subject is also referred to in the Russian letter in the July number of *Metal Progress*. Penetration of the waves, through 3ft. or 4ft. of steel, is mentioned. A discontinuity, not

exceeding two ten-thousandths of an inch in thickness, in the metal, produced by laying two accurately ground plates together in contact, was found to cut off the waves completely unless the ground surfaces were united by a film of oil.

Sokoloff's method of detection by the "sound-wave grating" makes use of an additive effect, and does not readily enable the location and size of individual defects to be determined. The method may be useful for guaranteeing the soundness of large bars or forgings, but a development of Mülhäuser's more portable apparatus would be more useful for general purposes. There are other methods of revealing supersonic waves; for example, if the metal surface is coated with transformer oil, ripples occur at the position at which the supersonic waves are emerging. In materials of moderate thickness, it is unlikely that the extremely sharp shadow-graphs produced by X-ray and γ-rays can be equalled by means of supersonic waves, and there is little hope of obtaining methods of detection as sensitive as the photographic method used in radiography. On the other hand, for large masses of steel, the supersonic method may have advantages. It is hardly possible to estimate yet whether an inspection of materials by means of supersonic waves will be of any technical use. Up to the present it is only the theoretical and practical possibility of such a process that has been demonstrated.

Hydrogen Penetration and Decarburisation of Steel.

WITH the growing importance of catalytic hydrogenation processes in which high temperatures and pressures are used, a great deal of research is being directed towards the development of suitable materials for the construction of the necessary apparatus. Not only must the steel have a strength capable of withstanding the high pressures and temperatures used, for example, in the synthesis of ammonia and in the hydrogenation of coal and oil, but it must also be resistant to decarburisation and penetration by hydrogen under the conditions of the work. At present the relatively expensive high-chromium steels are generally employed for this type of plant, but Baukloh and Guthmann* have recently shown that, contrary to the previous assumption, that a minimum of from 3 to 6 per cent. of chromium was necessary to prevent attack by hot, high-pressure hydrogen, actually steels with as little as 0·9 per cent. chromium can be considered to be resistant for all practical purposes, and that there appears to be a direct relation between the resistance to hydrogen and the carbon content of chromium steels. The same authors have recently studied† more fully the permeability of various steels to hydrogen and the extent to which decarburisation takes place at temperatures up to 900 deg. Cent.

In this work thick-walled tubes of various plain carbon and alloyed steels were drilled out from solid rods and mounted inside an evacuated quartz tube in an electrically heated furnace; hydrogen at pressures up to 60 atmospheres was then admitted to the steel tube and the rate at which it diffused into the quartz tube measured. Tests on plain steels with 0·015 to 0·88 per cent. carbon showed that the rate of diffusion at 600 deg. Cent. and 20 atmospheres pressure decreased exponentially with increase in wall thickness and below 700 deg. Cent. linearly with increase in the carbon content; as previously pointed out by Baukloh and Kayser‡ the diffusion is not continuous, but pulsating, the amounts diffusing per unit time oscillating by ± 20 per cent. about a constant mean value. The rate of diffusion increases with increasing grain size along an almost parabolic curve, and a similar type of curve expresses the relation between rate of diffusion and temperature up to the α–γ transformation point, above which there is an abrupt fall in the rate of diffusion for steels containing up to 0·7 per cent. carbon. These results indicate that, contrary to earlier suggestions, diffusion takes place through the actual grains and not solely along the grain boundaries which actually tend to retard instead of promoting diffusion. With increasing pressure the permeability of steel (0·88 per cent. carbon) to hydrogen increases at first according to the expression $m = K \cdot p^{\frac{1}{2}}$, but becomes constant at pressures greater than 120 atmospheres.

Addition of chromium to mild steel results in a rapid reduction of the permeability up to 1 per cent. chromium, then in a slow linear reduction up to 6 per cent. chromium, otherwise the steels behave in a similar manner to plain carbon steels.

When turnings of 0·88 per cent. carbon steel are heated in hydrogen the rate of decarburisation increases rapidly at first then more slowly with increase in pressure; in six hours decarburisation is complete at 900 deg. Cent. at 30 atmospheres, at 700 deg. Cent. at 60 atmospheres, and at 600 deg. Cent. at 90 atmospheres. With metal of thicker cross section the degree of decarburisation in a given time is approximately a parabolic function of the hydrogen pressure, and a similar function of the temperature up to the α–γ transformation point. In all respects, therefore, decarburisation closely follows hydrogen penetration, and it is obvious that there must be a close connection between the two phenomena in the case of carbon steels. With chromium steels, however, decarburisation is not so intimately connected with the hydrogen permeability, especially at high chromium contents; up to 0·7 per cent. chromium decarburisation falls slowly with increase in chromium, but there is a sharp and abrupt fall between 0·7 and 1 per cent. chromium and only a very slight linear fall with further increase in the chromium content. This behaviour is attributed to the greater stability of the carbides in chromium steels than in plain carbon steels.

The effect of other alloying elements on the decarburisation of steel has been investigated by Baukloh and Guthmann* by passing a rapid stream of hydrogen at atmospheric pressure over heated turnings of the metal. With up to 0·4 per cent. nickel the decarburisation increases with rise in temperature to 850 deg. Cent., then decreases slowly, but with 0·5–1·7 per cent. nickel there is a decrease in decarburisation up to 850 deg. Cent., followed by a very sharp increase. The decarburisation curves for manganese steels rise sharply between 700 deg. and 850 deg. Cent., then more slowly, the minimum decarburisation occurring with about 0·5 per cent. manganese. Addition of silicon, tungsten, molybdenum, vanadium, tin, and copper, appreciably reduces the rate of decarburisation of steel in hydrogen, especially at temperatures below 850 deg.

* *Arch. Eisenhüttenwesen*, 1935–6, 9, 201.

† *Zeitschrift für Metallkunde*, 1936, 28, 34.

‡ *Ibid.*, 1934, 26, 156.

Cent.; with molybdenum the minimum rate occurs at 0·3 per cent., and with copper at 0·6 per cent., whereas in all the other cases the rate decreases with increasing content of alloying element.

Tin-Base Bearing Metals.*

By PROFESSOR B. P. HAIGH.

Progress in aero and other engine design in recent years has indicated limits to the load and speed capacity of the white bearing metals that have long been employed with familiar success in wide fields of practice, and a great deal of scientific research has been carried out in this country and abroad to improve white metals, particularly in their capacity to resist cracking under severe pulsating loads combined with friction. A valuable paper by F. v. Göler and H. Pfister, of the Metallurgical Laboratory of the Metallgesellschaft A.G., Frankfurt a.M., published in *Metallwirtschaft*, is therefore of special interest.

The authors have carried out an interesting investigation of the mechanical properties of nine ternary alloys containing 2, 7, and 12 per cent. of antimony, and 3, 6, and 10 per cent. of copper alloyed with tin; and their description of the results is associated with a well-balanced analysis of data from other sources and a discussion of the practical significance of the conclusions. The results appear to be in close agreement with those of work done in the United States and this country, and compare in a most interesting manner with recent work done in this country by different investigators associated with the International Tin Research and Development Council.

It is apparent that the nine alloys have been selected to cover a wide field of investigation that requires more detailed study, but the present need for such a preliminary wide survey is urgent. The alloys containing 7 per cent. antimony lie on the border line between two distinct types of white metal, as those containing more antimony exhibit cubes of the somewhat harder SbSn constituent mingled with the softer matrix. Much of the value of the investigation lies in the contrast between these two classes of alloy.

The method of casting adopted by Göler and Pfister is one that admits of careful control, but is perhaps abnormal. The pieces were cast in bars of 30 mm. diameter in one arm of a V-shaped steel mould arranged for pouring through the opposite arm. The arrangement necessitated a rather high pouring temperature, 500 deg. Cent., with the mould at 200 deg. Cent., and on this account the mechanical strength values may be somewhat lower than might have been recorded by other methods.

The mechanical tests employed include tensile and compression, Brinell, bending, notched-bar, abrasive wear, and fatigue, and the results are compared in a series of diagrams. The tensile tests show increase in strength and reduction of elongation with progressive alloying, but it may be doubted whether the apparent brittleness of the highly alloyed samples, as shown in the tensile test, is really of primary importance in bearings subjected to very different conditions of loading. Tensile strength, nevertheless, appears to afford a valuable indication of the resistance that may be expected to cracking in fatigue tests. Compression tests were made on cylinders, 20 mm. in length, and in diameter relatively shorter than the two-diameter cylinders that have been used in recent work in this country. It is notable that the authors have endeavoured—even in these compression tests—to focus attention upon resistance to cracking. Instead of measuring the maximum loads reached in the compressive tests, they record the values at which cracks appeared on the bulging surfaces of the cylinders. Brinell values are given for tests at 20 deg. and also at 150 deg. Cent., and reference is made to Greenwood's recent work in which cracking was studied under widely different conditions of pounding. The results of the bending tests on pieces without notches conform closely with those of the tensile and compression tests. Fatigue tests were carried out in a Schenck machine, and appear to confirm results obtained by other methods used in this country, and to conform to the changes of strength indicated in tensile and other tests.

In general, the several mechanical tests, excluding only abrasive wear, indicate increasing strength with increase of antimony from 2 to 7 per cent., with little or no further increase above that stage up to 12 per cent. Thus in these respects the presence of the SbSn cubes in the antimony-rich alloys does not appear beneficial. This conclusion, which is quite in agreement with the results of other investigations, requires, however, much further work on intermediate alloys to define the position more precisely. The relation between strength and antimony content is of great practical importance, and requires further study in view of the recent work of Hanson and Pell-Walpole, described this year in a paper contributed to the Institute of Metals. These authors have shown that under conditions of equilibrium, tin can retain only 3·5 per cent. of antimony in solid solution at room temperature. The solubility increases gradually with rise in temperature to 4 per cent. at 190 deg. Cent., after which the increase is rapid.

Copper appears to increase mechanical strength progressively in all proportions up to 10 per cent., but induces brittleness with peculiar characteristics that deserve further investigation. In compression tests in particular, the copper-rich alloys exhibit a capacity for "work softening," as distinct from the work hardening that is such a familiar characteristic of most ductile metals. When a compression test piece of such an alloy is gradually crushed, it offers increasing resistance only up to a certain stage, beyond which its resistance decreases, although the cross-sectional area continues to increase by bulging. The action has been studied also in this country and appears to be characteristic of copper-rich tin-base alloys. It may be borne in mind that these contain a feathery framework of hard and brittle CuSn, and it is believed that this framework reinforces the strength of the alloy only so long as it remains intact. When deformed beyond a certain stage, the broken fragments are less effective as reinforcement, and the alloy loses strength progressively towards a lower limit corresponding to that of the soft matrix.

The abrasive wear tests carried out by Göler and Pfister were made by friction on dry emery paper with a load of 1 kilo. on the end of a rod of 2 mm. diameter. The authors express the opinion, based on experience, that this test has an orienting value for wear under practical conditions of service in engines. Increase of copper reduces resistance to wear in quite marked degree, while antimony has little effect up to 7 per cent., and in greater amounts causes increase of wear.

* Review abstract and discussion of a paper by F. v. Göler and H. Pfister, *Metallwirtschaft*, 1936, 15, 342–348 and 365–368.

In discussing their work in relation to other investigations, the authors refer to the effect of lead on tin-base bearing metals. Lead increases the solubility for antimony and hardens the alloys at ordinary temperatures, but renders the CuSn structure coarser (Karelitz and Ellis). The harmful effects of lead occur at high temperatures, and are due to the formation of the ternary eutectic of tin, antimony, and lead, which melts at 180 deg. Cent. Although this latter temperature may appear high, it is not high enough to leave the margin required for current conditions of service.

After mentioning the influence of nickel—which appears to be slight and disputed—the authors refer to the use of cadmium, which has given results of great promise. Cadmium dissolves in the ground mass of the grains, raising the strength by 10 to 20 per cent. in a manner that is effective at relatively high temperatures. The authors refer to the investigations on cadmium alloys carried out independently in this country and in Germany, and published in 1934 and 1935 respectively. It is much to be hoped that further work will be undertaken to study the effect of cadmium in selected copper-antimony alloys with tin-base. The authors do not appear to have investigated the self-annealing properties that constitute such a characteristic feature of the tin-base bearing metals, but the practical advantages of the high-tin alloys are recognised repeatedly and these alloys are recommended in the light of investigations and experience.

The Iron-Aluminium-Carbon System.

THE study by R. Vogel and H. Mäder* of the iron corner of the constitutional diagram of the iron-aluminium-carbon alloys has revealed a very complicated system.

The experimental alloys were made from pure materials melted in argon, the iron being melted first, the carbon then added, and finally the aluminium. The range of compositions covered was up to 5 per cent. of carbon and 40 per cent. of aluminium, and the constitution of the alloys was studied by means of heating and cooling curves and microscopical examination.

Details of the two binary systems, iron-carbon and iron-aluminium are relatively well known, but the only feature of the aluminium-carbon system which has been established is the existence of the compound Al_4C_3 with 25 per cent. of carbon.

Vogel and Mäder have drawn up an ideal diagram, and on the basis of a relatively small amount of experimental work in comparison with the magnitude of the problem have checked it at various points to give it a quantitative actuality. The sections are too complex to be easily intelligible if reproduced in part in an abstract, and yet in some respects it is possible that the diagram of the system has been unduly simplified. For example, the transformation which is known from the work of Sykes and Evans to occur in the neighbourhood of the composition corresponding to Fe_3Al in the aluminium-iron alloys finds no counterpart in the system proposed by Vogel and Mäder.

The simplest of the sections are reproduced in Figs. 1 and 2, and give an indication of the structure of the alloys of low aluminium or low carbon content, and of their probable response to heat treatment.

Aluminium forms a closed gamma-loop with iron. Gamma-iron is not formed in the presence of more than 1·2 per cent. of aluminium, but, as usual, its

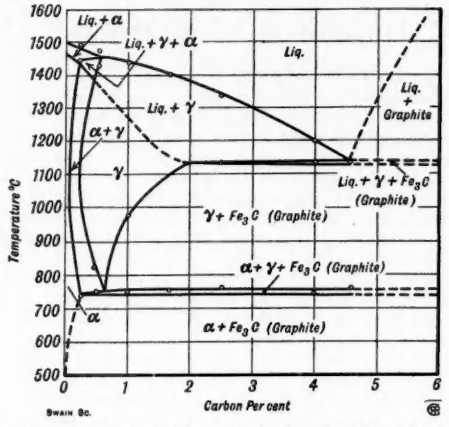

FIG. 1—*Constitutional Diagram of Iron-Aluminium-Carbon Alloys containing 2 per cent. of Aluminium.*

stability is extended to a higher percentage in the presence of carbon. Alpha and gamma iron are present as ternary solid solutions of aluminium and carbon in iron. The A_3 point is raised and the A_4 point lowered by increase in aluminium. The beginning of Ac_1 is also raised by increase in aluminium, and

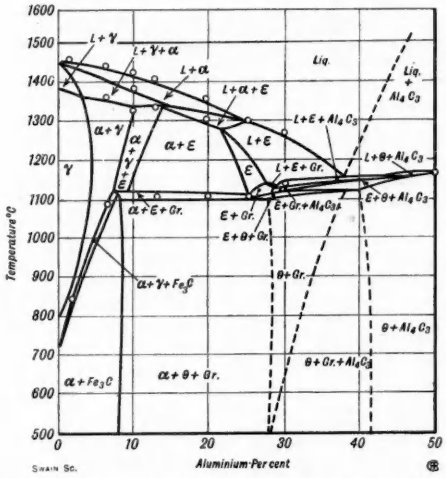

FIG. 2—*Constitutional Diagram of Iron-Aluminium-Carbon Alloys containing 0·5 per cent. of Carbon.*

the point is extended into a temperature range, the top of which reached 1100 deg. Cent. with 7 per cent. of aluminium.

The epsilon-phase (Fig. 2) is a solid solution of carbon in the compound $(FeAl)_n$, and the theta-phase a solid solution of carbon in the compound $FeAl_2$. These four (α, γ, ε and θ), together with

* *Archiv für das Eisenhüttenwesen*, Jan., 1936, 1935–36, 9, 333

graphite and Al_4C_3 constitute the six primary crystal phases of the system.

The addition of aluminium above a certain amount leads to graphite separation. This is usually an irreversible change, and therefore an effect which immediately introduces uncertainty in the equilibrium relations of the iron carbide, though the authors state that in this system, with iron and carbon in definite proportions, no alteration in the amount of graphite precipitated could be observed with further increase in aluminium content.

The paper may be regarded as a skilful deduction of the possible phase relationships of the iron-aluminium-carbon alloys, but it seems likely that an intensive study of selected ranges of composition may lead to substantial revision of the details.

The Energy Absorbed in the Deformation of Steel.

IT is well known that the heat generated when a metal is subjected to plastic deformation is less than the thermal equivalent of the mechanical work expended. Some energy is absorbed by the metal in the process, or, in other words, some of the heat

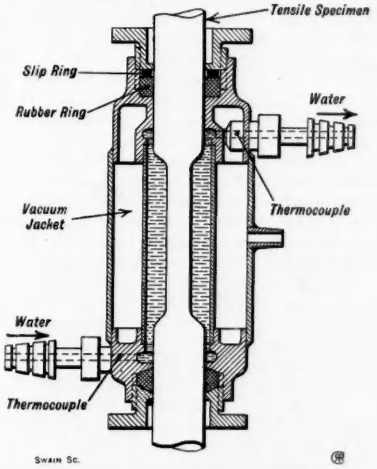

FIG. 1.—*Flow Calorimeter for Estimation of the Heat Changes during a Tensile Test.*

becomes latent. This change in the internal energy of the material is of great theoretical interest, and numerous attempts have been made to measure it.

At one time it was supposed that a very large percentage of the work done was rendered latent, figures like 70 to 90 per cent. being suggested.[1] Giraud[2] found 70 per cent. for the proportion of energy rendered latent by the cold-drawing of steel wire, but such high results are almost certainly due to experimental error. By means of tensile tests, Hort[3] obtained values ranging from 5 to 15 per cent. for soft iron, and Farren and Taylor[4] 13½ per cent. for mild steel containing carbon 0·17, manganese 0·76 per cent. Determinations made on tensile specimens are not beset by such uncertain corrections as those on wire drawing, which, however, when carried out with extreme care tend to confirm the results of the tensile tests.[5] Experimental difficulties are in any case so great that as many independent measurements as possible are to be welcomed.

The latest work on this subject has been carried out by H. Esser, H. Cornelius, and W. Banck,[6] and reported under the title "Investigations of the Heat Change in the Tensile Test on Steel Specimens."

The tests were made in a specially designed flow calorimeter, the details of which are sufficiently indicated in Fig. 1. The calorimeter operating in conjunction with a thermostat was calibrated by fitting a model test piece with internal heating elements and determining the rise in temperature for a given input of energy. The error of measurement was found to be less than 1 per cent.

As a preliminary the heat change during elastic

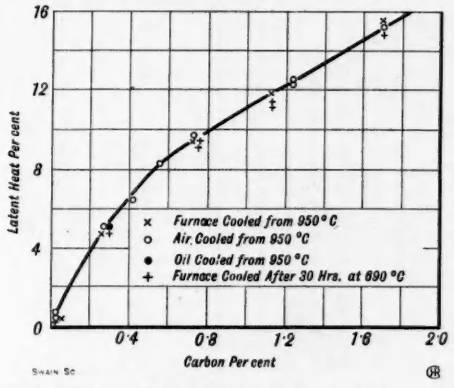

FIG. 2.—*Heat Rendered Latent in Relation to Carbon Content After Different Heat Treatments.*

deformation was measured on a steel containing carbon 0·39, silicon 0·23, manganese 0·88, phosphorus 0·046, and sulphur 0·041 per cent., the "elastic limit" (*i.e.*, 0·003 per cent. permanent extension), of which was 22½ tons per square inch. The heat change below the elastic limit is, of course, as pointed out by Thomson in 1853, an absorption of heat on loading and an evolution of heat on unloading. By experiments, both in loading and in unloading, the present authors obtained mean values of −0·283 cal./cm.³ and +0·282 cal./cm.³ respectively.

The study of the heat change during plastic deformation was carried out on a series of fourteen steels. These steels were subjected to a tensile test inside the calorimeter. The latent heat was estimated by subtracting the heat given up by the bar, and determined calorimetrically, from the thermal equivalent of the work expended in deformation, which was ascertained from the recorded stress-strain diagram.

[1] W. Rosenhain, "Metals," in Glazebrook's "Dictionary of Physics," Vol. V, page 398.

[2] R. Giraud, *Revue de Métallurgie*, 1928, 25, 347.

[3] H. Hort, *Forsch. Ing.-Wes.*, 1907, 41, 1; *Zeit. V.d.I.*, 1906, 50, 1831.

[4] W. S. Farren and G. I. Taylor, "Proc.," Royal Soc., 1925, 107A, 422.

[5] W. Rosenhain and V. H. Stott, "Proc.," Royal Soc., 1933, 140A, 9.

[6] H. Esser, H. Cornelius, and W. Banck, *Archiv für das Eisenhüttenwesen*, April, 1936, 1935/36, 9, 529.

The seven carbon steels (carbon 0·1 to 1·7 per cent.) were tested in four different conditions of heat treatment, but these differences were without effect on the percentage amount of heat rendered latent. In Fig. 2 this percentage is shown in relation to the carbon content of the steel. The percentage of the heat equivalent of the total work of deformation rendered latent was very small for electrolytic iron (only about 0·26 per cent.), but with increasing carbon content it rose, first quickly and then at a slower rate. These results show that it is not admissible to refer to the energy absorbed by a material (*e.g.*, steel or brass) without specifying the composition. In a further study of the effect of composition it was found that in a 14 per cent. chromium steel with 0·1 per cent. carbon about the same amount of heat is rendered latent (viz., 1·8 per cent.) as in a carbon steel of the same carbon content. The chromium steels of higher carbon content showed distinctly lower values than the corresponding carbon steels, but the

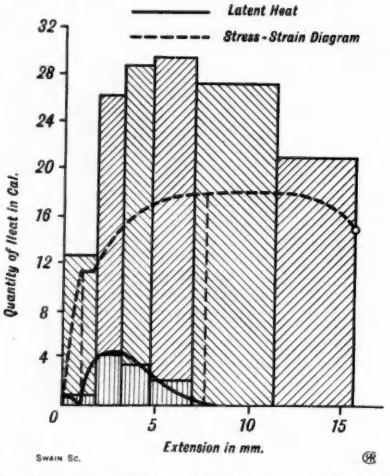

FIG. 3.—*Heat Rendered Latent in Relation to the Stress-Strain Diagram.*

low-carbon, chromium-nickel austenitic steels lay a little above the carbon steel curve. No definite conclusion as to the effect of alloy additions was reached.

In order to ascertain in what part of the stress-strain diagram the work of deformation was not fully converted into heat, experiments were carried out on normalised carbon steels and on annealed steels containing granular cementite. Both series of experiments, in which the heat change was determined in stages of increasing load, gave results of the type indicated in Fig. 3. The whole shaded area represents the heat equivalent of the work expended in deformation while the vertically shaded areas represent, on the same scale, the amount of heat rendered latent at each stage of loading. The region of the stress-strain diagram in which energy absorption occurs begins just above the elastic limit, and ends before reduction of area sets in. The greatest proportion of energy is rendered latent just above the yield point. This leads to the conclusion that there is no relation between degree of strain hardening and the heat rendered latent, as Hort supposed. Strain hardening continues beyond the stage at which reduction of area begins, though only over a limited part of the gauge length, but the authors claim that if any appreciable amount of heat had become latent during reduction of area, their apparatus was sufficiently sensitive to ensure that it would not remain unobserved. Furthermore, the heat rendered latent bore no relation to the degree of strain hardening of the different steels, while it increased with carbon content, whereas capacity for strain-hardening decreases.

It has been suggested that the heat rendered latent represents the formation of amorphous material from the crystalline mass; in other words, that the increase in energy content is due to a phase change in the material. This explanation is not supported by the theoretical views of the authors. They allow that the formation of slip-planes accounts for part of the energy which does not appear as heat, but for the rest they attribute the increased internal energy of the material to the existence of highly localised systems of internal stresses which are produced over closely adjacent regions throughout the mass.

A New Method of Polishing Metallic Surfaces.

THE polishing of metals for micro-examination involves rubbing on a series of emery papers of progressively finer grade, and finally polishing on a damp cloth dressed with polishing powder. The process requires time and skill, and it has the important drawback, the seriousness of which varies with the metal and the skill of the polisher, of being liable to alter the micro-structure of the surface layer so that, even after etching, the structure seen may not be representative of the metal below. This danger is specially great with soft metals.

An electrolytic method of polishing, which removes the mechanical disturbance of the surface caused in the preliminary smoothing of the metal, has recently been developed. It deserves the serious attention of metallurgists for its possible significance in metallography, and in the investigation of processes in which the surface condition of the metal may have an important bearing on its behaviour—for example, corrosion and fatigue. The method consists essentially in treating the metal, previously smoothed by rubbing on two or three grades of fine emery paper, as anode in the specified solution, usually for 10–15 minutes, washing and drying. The degree to which the surface has been initially smoothed generally determines the time of anodic polishing required. The longer the anodic treatment is continued, the greater is the depth of metal removed, and it is thus possible to expose metal which has not been affected by the preparatory mechanical processes of cutting and smoothing. Details of the method and of its application to various metals, given below, are derived from publications by P. Jacquet.[1, 2, 3] Photomicrographs of copper polished with alumina and by the electrolytic method are shown in Figs. 1 and 2 respectively.

Jacquet[4] has used the anodic polishing method to study the effect of the mechanical polishing process on the structure of the surface layers of brass. He built up a mechanically polished brass surface with electro-deposited copper (to preserve the edge on subsequent sectioning), and examined an anodically polished section under the microscope. The micro-structure was found to be affected to a depth of

about $4–6 \times 10^{-3}$ mm. by the emery polishing. This layer recrystallised on heating to 280 deg. Cent. for one hour. Jacquet relates these observations to those of Hothersall[5] who found that a surface layer of similar thickness was weakened mechanically by polishing brass on emery paper. These results emphasise the important effect which may be produced by mechanical treatments on the structure and properties of surfaces.

DETAILS OF METHOD.

The specimen, suitably smoothed on the surface by mechanical means and degreased with organic

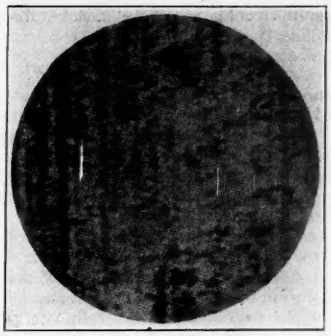

FIG. 1

solvent, is inserted horizontally in the electrolyte, the face to be polished uppermost, with a cathode of copper sheet, 8–10 mm. above it. The specimen may be arranged vertically, but a higher current density is required for polishing. The under surfaces of the specimen are "stopped-off" with a suitable lacquer, leaving an area, say, 1 cm. by 1 cm., exposed. The cathode area may be 8–10 square centimetres.

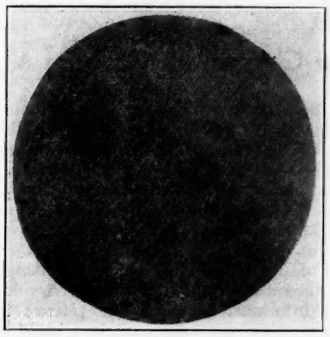

FIG. 2

A diagram showing the arrangement of the bath and electrical circuit is given in Fig. 3.

To obtain the best results, it is necessary to brush off any bubbles which cling to the specimen when it is inserted in the solution. The solution tends to become contaminated with particles of metal deposited in powdery form on the cathode, and it should be kept clear by filtration. It should also be thoroughly stirred before each electrolysis to remove small bubbles of gas which are formed at the cathode and tend to produce an emulsion in the viscous liquid.

The process is controlled by voltage, a curve (typical of copper in phosphoric acid) relating voltage and current density being given in Fig. 4. Up to point C, the anode dissolves with a matt surface; above C′ the surface becomes smooth and polished in appearance. At D the evolution of gas bubbles commences, and near D the polished appearance of the specimen is marred by numerous points or dots caused by adherent gas bubbles: with more vigorous evolution of gas, corresponding to a higher current density, a smooth polished appearance is again attained.

TREATMENT OF COPPER AND α BRASS.

An electrolyte containing 530 g. per litre of pyrophosphoric acid ($H_4P_2O_7$) is used at room temperature (15–25 deg. Cent.). If the preliminary smooth-

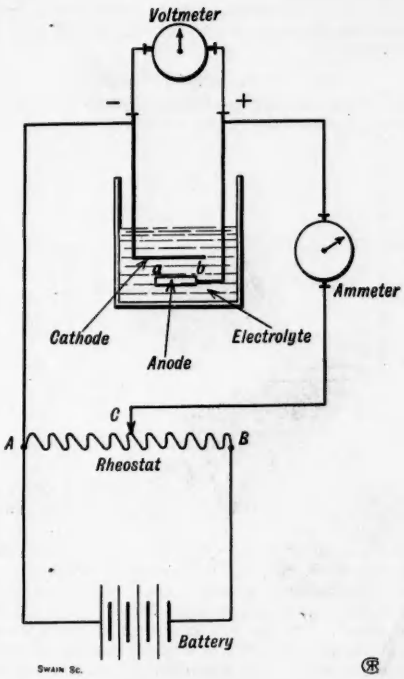

FIG. 3

ing has been carried to No. 00000 emery paper, a treatment of 10–15 minutes is needed. Under these conditions, the optimum voltage V_3 (Fig. 4) is about 1·90 volts; V_2, the point at which gas evolution starts, is about 2·10 volts. At the optimum voltage the current density with a horizontally arranged anode is about 6 amperes per square dm. for copper and 13–15 amperes per square dm. for brass; with a vertically arranged copper anode, a current density of 9·5 amperes per square dm. is needed for polishing under the same conditions.

Any whitish film present after washing and drying may be removed by immersion in a dilute solution of phosphoric acid.

To develop the structure, the specimen may be etched in the normal way, or it may be replaced in

the electrolyte and treated for a few seconds at a current density of 1–1·5 amperes per square dm.

α+β BRASS.

The solution described above is used at the same voltage (1·90 volts, corresponding to a current density of 9–11 amperes per square dm.). A brilliant surface cannot be obtained with this type of brass, nor with α brass containing high percentages of iron or lead. The treatment described, however, produces a smooth surface, free from scratches and showing the structure of the metal. The structure may be further developed by brief treatment in the solution at low current density.

BRONZE.

A solution containing 990 g. per litre of orthophosphoric acid (H_3PO_4) is recommended, a low current density of 1–2 amperes per square dm. being used. The results are less satisfactory than for copper or α brass, and it is difficult to remove all scratches, since the time of treatment must be limited because of the selective attack of the different constituents.

LEAD, TIN, LEAD-TIN ALLOYS.

The anodic polishing of these metals has not been extensively studied, but procedures for polishing them

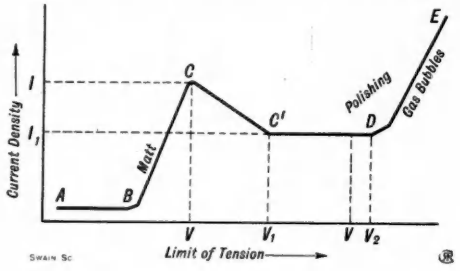

FIG. 4

are described. A mixture of 650–750 cc. glacial acetic acid and 250–350 cc. perchloric acid solution (55 deg. Bé) is used as electrolyte.

Lead is subjected to three successive treatments at a current density of 20–25 amperes per square dm., with intervening washing and drying:—(1) For 1–2 minutes: a brown skin forms which must be washed off. (2) For 3–5 minutes: the scratches are removed, but the metal is severely attacked. (3) For a few seconds: the specimen is carefully watched and removed as soon as it assumes a brilliant appearance. The structure may be developed by a slight extension of the third electrolysis, by a subsequent anodic treatment at low current density or merely by exposing the specimen to the air. The solution requires frequent renewal, too high a concentration of lead causing crystalline outgrowths from the cathode.

Tin is treated at 15–17 amperes per square dm., the structure being developed by subsequent electrolysis at 1–2 amperes per square dm. for a few seconds.

Lead-tin alloys can also be treated in this electrolyte, but difficulties similar to those found with bronzes are encountered. A low current density is said to lessen the degree of selective attack.

MECHANISM OF THE ANODIC POLISHING OF COPPER.

Jacquet suggests[3] that the conditions favourable to the anodic polishing of copper result in the production of a dense film of liquid about 0·05 mm. thick on the surface of the metal. This film is assumed to have a high electrical resistance. Consequently, projecting points on the surface receive a higher current density and are therefore dissolved at a more rapid rate than the surrounding surface. The surface is thus automatically levelled. It follows that for successful anodic polishing, the products of anodic dissolution must be soluble in the electrolyte to give a film of the required properties. In support of this suggestion attention is drawn to the behaviour of metaphosphoric acid, which is unsuitable as an electrolyte for the anodic polishing of copper. Its copper salts are insoluble both in water and in the acid, whereas the copper salts of both ortho and pyrophosphoric acids, which are suitable for polishing, are soluble in the respective acids.

LIMITATIONS OF THE METHOD.

The anodic polishing process has been stated to be applicable to aluminium, nickel, lead, and molybdenum,[6] as well as to copper, brass, and tin. It will be recalled that numerous references have recently been made in the patent literature to the anodic polishing of aluminium in connection with its use for the specular reflection of light.

It would appear, however, that the process is less suitable for the treatment of alloys having a complex structure, because of the probability of a differential rate of solution of the various constituents. Difficulty is also likely to be experienced in the presence of non-metallic inclusions. It therefore appears probable that any applications of the process will be limited to relatively pure metals, and to certain homogeneous solid solution alloys.

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[1] P. Jacquet, *Nature*, 1935, 135, 1076; *Comptes Rendus*, 1935, 201, 1473; *Génie Civil*, 1936, 108, 92.
[2] P. Jacquet, *Trans. Electrochem. Soc.*, 1936, 69, Preprint 2.
[3] P. Jacquet, *Bull. Soc. Chim.*, 1936, 705–723.
[4] P. Jacquet, *J. Chim. Phys.*, 1936, 33, 226–231.
[5] A. W. Hothersall, *J. Electrodepos. Tech. Soc.*, 1932, 7, 115.
[6] Fr. Pat. 707,526 (1930).

Iron-Chromium-Carbon Alloys.

THE constitution of the iron-chromium-carbon alloys has been made the subject of intensive study by Dr. W. Tofaute, of Essen, and a number of his associates during the past five or six years.

A section of this work was reviewed in THE METALLURGIST last August, and a further instalment has now appeared under the title of "The System Iron, Chromium, Chromium Carbide Cr_7C_3, Cementite,"* by W. Tofaute, C. Küttner, and A. Büttinghaus.

The diagram proposed has been developed from existing information about the phase-relationships in the binary systems concerned, by the aid of thermal, microscopic, and other physical methods, including X-ray analysis of the structures. The investigation was carried out on alloys containing up to 70 per cent. of chromium and a carbon content corresponding to the mixed carbides Fe_3C and Cr_7C_3, which are shown by crystallographic data to possess a limited range of mutual solid solubility.

The authors refer in appreciative terms to the summary of information on the binary systems of chromium and on the iron-chromium-carbon system

* *Archiv für das Eisenhüttenwesen*, June 1936, 1935/6, 9, 607.

contained in the D.S.I.R. publication on " Chromium Steels," by Dr. R. H. Greaves,† which has enabled them to dispense with detailed references except to work reflecting the latest state of knowledge or necessary to the formulation of the ternary system.

In the interpretation of the constitution of the alloys, the existence of the carbides Fe_3C, $(CrFe)_7C_3$ and $(CrFe)_4C$ was accepted on the basis of the work of previous investigators, and that of FeCr in accordance with the iron-chromium diagram of Wever and Jellinghaus.

The constitution at room temperatures is represented in Fig. 1. In general form this resembles the diagram of Westgren, except that it is further complicated by the existence of a break in the series of iron and chromium solid solutions, due to the existence of FeCr.

Typical sections of the complete diagram, representing alloys with 12, 15, 20, and 30 per cent. of chromium, are shown in Figs. 2 to 5, but the original paper contains many more sections and should be consulted for greater detail and for indications of the experimental evidence on which they are based.

For practical purposes the valuable part of the diagram is the low carbon region. The solubility of carbon in the α solution just below the solidus (*i.e.*, δ region) is shown as about 0·1 per cent. in the 12 per cent. chromium steel, increasing to perhaps 0·2 per cent. with 20 to 30 per cent. chromium and then falling again. The solubility of carbon in the 12 per cent. chromium α solid solutions at about 800 deg. Cent. is very small. The Ac_1 point of the 12 per cent. chromium-iron alloy is shown at about 820 deg. Cent., falling to a little under 800 deg. Cent. as the carbon increases to 1·3 per cent. The γ field does not reach down to this temperature. It is bordered by two phase fields (α+γ, and γ+carbide), but, below it, there is a three-phase

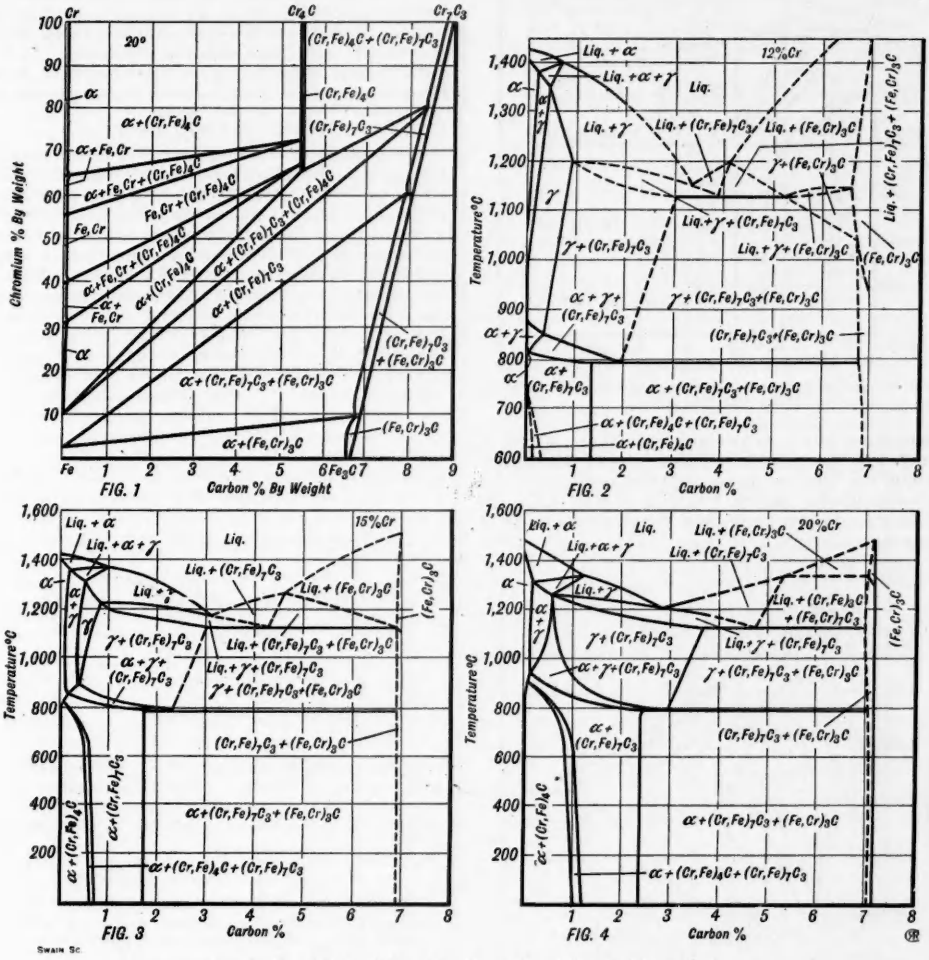

FIG. 1—*Constitution of Iron-chromium-carbon Alloys at 20 deg. Cent.*
FIGS. 2–4—*Sections Across the Iron-chromium-carbon Diagram.*

† References to the work of other authors mentioned in this review will be found in this book.

field ($\alpha+\gamma+$carbide), indicating that hardening at the eutectic composition occurs, not suddenly, but gradually over a range of temperature. The authors state that these transformations can be clearly established by the help of dilatation measurements and quenching-temperature/hardness curves. Such

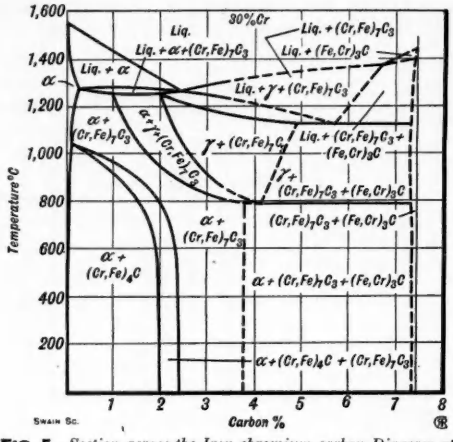

FIG. 5—*Section across the Iron-chromium-carbon Diagram at 30 per cent. Chromium.*

observations are in accordance with those of Monypenny, who has pointed out that part of the carbide forming the pearlite in an annealed chromium steel does not dissolve at Ac_1, but progressively goes into solution in passing through a considerable range of temperature above this point. This effect, which

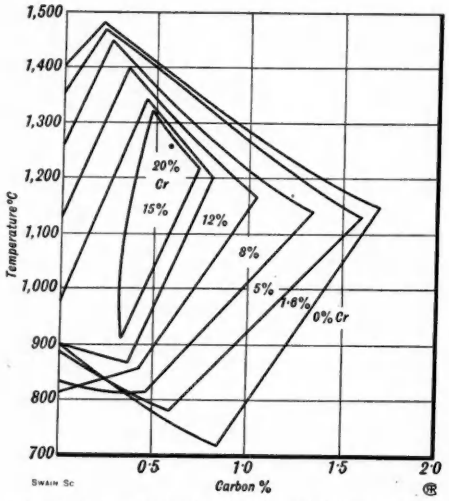

FIG. 6—*Projection of γ Regions in Alloys of Different Chromium Content.*

Monypenny ascribed to structural differences in the carbide, is now interpreted as being due to the gradual shift of the equilibrium as the alloy is heated through a three-phase field ($\alpha+\gamma+$carbide).

The raising of the Ac_1 point and narrowing of the γ phase field with increase in chromium content, is shown by comparison of Figs. 2 to 5, and so also is its final disappearance at 20 per cent. chromium, followed by the displacement of the remaining fields containing the γ phase to a carbon content exceeding 1 per cent. in the 30 per cent. chromium alloy. At this chromium content, with carbon below 1 per cent., the alloy consists at all temperatures wholly of α solid solution and carbide $(CrFe)_7C_3$ or $(CrFe)_4C$, and is no longer in any degree hardenable. These alloys can, therefore, show no distortion due to hardening stress on repeated heating and cooling, a fact which enhances their value in the cast condition for heat-resisting purposes.

In further commenting on the diagrams, it will be convenient to deal with certain features separately.

LIMITS OF THE γ REGION.

The γ phase field is displaced to a higher temperature and a higher carbon content with increase in chromium. The form of the γ region in alloys of different chromium content is made clear in Fig. 6, in which the γ phase area is projected on to the iron-carbon plane. With increasing chromium the single-phase field continuously shrinks in size until with 20 per cent. chromium the homogeneous region has disappeared. To secure alloys which will give the highest possible hardness after quenching, a carbon content lying within the appropriate field must be chosen. If the carbon is above this limit, free chromium carbide is formed and takes no part in the hardening. If it is below the limit, ferrite is in equilibrium with the γ solid solution at the quenching temperature and the quenched alloy remains heterogeneous and is only partially hardened. From this diagram also it is possible to read the values of

(i) Maximum solubility of carbon in the γ solid solution.

(ii) Carbon content of the eutectoid.

Chromium, per cent.	Maximum solubility of carbon in austenite, per cent.	Carbon content of the eutectoid, per cent.
0	1·7	0·85
1·6	1·6	0·6
5	1·3	0·45
8	1·05	—
12	0·8	0·35
15	0·7	0·3
20	0·6	(0·6)

These values, given above, are in good agreement with those of several other investigators. The increase in carbon content of the eutectoid containing more than 15 per cent. chromium is well supported by microscopical evidence.

THE COMPOUND FeCr.

The fact that two compounds were long ago proposed on inadequate evidence ($FeCr_2$ by Monnartz, and Fe_2Cr by Fischbeck) has made metallurgists cautious in accepting the existence of FeCr. The magnetic investigation of Murakami led to the conclusion that iron and chromium formed an unbroken series of solid solutions at room temperature, and Adcock failed to get evidence of a compound by X-ray analysis. Adcock's alloys, however, showed magnetic anomalies in this region, and the existence of a compound was not finally disproved. An intermediate phase corresponding to the formula FeCr first appeared in the diagram of Wever and Jellinghaus, and its existence has since been confirmed by the X-ray investigations of S. Eriksson.*

The X-ray analysis of Tofaute, Küttner, and

* *Jernkontorets Annaler*, 1934, 118, 530.

Büttinghaus shows the presence of a constituent which they identify as FeCr in chromium alloys with 40 to 60 per cent. of chromium, and magnetic tests, conductivity and hardness confirm the presence of a phase which may pass in and out of solution in the groundmass in response to various heat treatments.

The possibility is not entirely removed that this phase is due to impurities. Adcock failed to track it down to nitrogen. On the other hand, the alloys used by Tofaute, Küttner, and Büttinghaus were not of high purity. The high-chromium alloys contained manganese and silicon in amounts which reached 0·5 and nearly 2·0 per cent. respectively, and the compound may not be entirely one of chromium and iron. Whatever the ultimate conclusion, any commercially produced alloy of the range 40 to 60 per cent. chromium, which might be expected to show very good corrosion resistance, is likely to be so strongly affected by a marked brittleness due to precipitation of the alleged FeCr that its practical application would necessarily be very limited. So large an amount of this phase is precipitated on annealing a 50 per cent. chromium alloy below 950 deg. Cent. that the material can readily be pounded into a fine powder.

This work of Tofaute and his colleagues, taken as a whole, must rank as the most valuable contribution made in recent years to the interpretation of the constitution of the iron-chromium carbon alloys. No doubt it will require revision; in particular, the use of pure materials may entail important changes, but meanwhile it will serve as an invaluable guide to the behaviour and properties of commercial high-chromium alloys and chromium steels.

Methods of Welding Aluminium and its Alloys.

MOST of the important developments in welding have resulted from long and patient work. It is therefore a difficult task to review recent progress without considerable reference to history, and so Monsieur Douchement, in a recent paper,* finds that it is necessary to look back as far as 1904, when Odam produced his flux, to perceive in true perspective the field of aluminium welding. In this paper the useful jointing methods for aluminium and its alloys, fusion welding by blow-pipe and arc, and electric resistance welding are discussed.

In blow-pipe welding the flux is all important, and the greatest care is necessary to obtain adequate drying, grinding, and mixing of its constituents, generally alkali chlorides, fluorides, and sometimes bisulphates. The choice of filler rod material depends on the composition of the parent metal and the purpose for which the finished article is intended. Where corrosion resistance is important, chemical homogeneity of the joint is approached as nearly as possible, and even the addition of titanium to the filler rod to reduce the grain size of welds in pure aluminium is not recommended for chemical work. For the complex alloys, however, homogeneity can only be obtained at the expense of poor mechanical properties and a tendency to cracking during cooling.

* Jacques Douchement, *Revue de Métallurgie*, March, 1936, Vol. 33, page 189.

A 4–5 per cent. silicon alloy rod may be used for many alloys; it has good fluidity and resistance to corrosion, small solidification contraction, and freedom from hot-shortness. It is not suitable, however, in cases in which heat treatment after welding is necessary, since it is not itself strengthened by such treatment, and, moreover, it produces an intermediate zone of low strength. Table I shows the

TABLE I.

Composition of filler rod.	Tensile strength in kilogrammes per square millimetres.			
	As welded.	Hammered weld.	Weld heat treated.	Weld hammered and heat treated.
99 per cent. Al	11·4	16·8	16·3	14·4
Al+4 per cent. Si	16·7	16·8	23	21
Al+0·6 Si+0·4 Mg	13·8	14·7	24·1	21
Al+1 Si+0·6 Mg+0·7 Mn	16·9	16	31·9	30
Al+2·5 Si+0·6 Mg+0·7 Mn	14·5	16·7	31·7	30·9
Al+4 Mg+0·5 Mn	15·8	16·3	28·5	25·4
Al+2 Mg+1·8 Mn	15·3	16·7	30	22

effect of varying filler rod composition on the strength of oxy-acetylene welds in Anticorodal (Si 1, Mg 0·65, Mn 0·7 per cent.), which has in the unwelded condition a tensile strength of 32–34 kilos. per square millimetre. It will be noticed that thermal treatment is only advantageous when the filler rod is composed of an age-hardening alloy.

Acetylene is the most popular fuel gas for welding aluminium and its alloys, but hydrogen is still used for thin material, and experiments have been made with other gases. Methane, for example, has been used in U.S.S.R. Interesting results have also been obtained by the Office Centrale de la Soudure Autogène with an air-acetylene flame surrounding the oxy-acetylene welding flame, in order to prevent oxidation. Table II shows the results which may be

TABLE II.

	Condition of weld.	Tensile strength, kg./mm.²	Elongation, p.c.
Hard aluminium	Untreated	8–10	12–15
,, ,,	Hammered	10–12	5–8
Aluminium-manganese alloy	Untreated	11–12	10–15
Almasilium	,,	15–18	4–6
,,	Heat treated	22–26	10–12
Duralumin	Untreated	18–24	2–3
,,	Heat treated	24–28	2–3
,,	Hammered and heat treated	30–35	5–10
7 per cent. magnesium alloy	Untreated	28–30	12–15

expected from welds in various aluminium alloys. The 7 per cent. magnesium alloy is particularly to be noted for its strength in the welded condition, compared with a figure of 30–35 kilos. per square millimetre and 15–20 per cent. elongation for annealed sheet. This alloy would appear to be extremely interesting from the welding point of view.

The concentrated heat of the arc reduces the extent of the annealed zone of low strength at each side of the weld. The carbon arc is principally used in repair work on castings, but the metallic arc with coated

electrodes is becoming of wide application. In addition to the duties of the flux in blow-pipe welding, the electrode coating must protect the metal passing through the arc and reduce its surface tension, and must ionise the arc gap in order to preserve arc stability. Recent developments are the Zack process, in which a three-phase supply is used, one phase being connected to the work, one to a carbon, and the third to a metallic electrode; and the atomic hydrogen process, in which molecular hydrogen is split up in a tungsten arc, and its heat of re-formation utilised for welding.

It is in the field of electric resistance welding that the greatest development has taken place during the last few years. Monsieur Douchement enumerates the difficulties presented by aluminium as :—

(1) High conductivity and high total heat of fusion make it necessary to use greater currents than are used for steel.

(2) The high heat conductivity causes waste of energy and detrimental heating of the area surrounding the weld.

(3) The high electrical conductivity makes the resistance of the material itself negligible compared with that of the three interfaces, electrode-aluminium, aluminium-aluminium, and aluminium-electrode.

Machines for welding aluminium are thus required to have large transformer capacity and extremely fine and consistent control of current, time, and electrode pressure. Of the various methods used to fulfil these requirements, Monsieur Douchement describes the Sciaky pressure control and accumulation of energy principle, the mercury vapour tube controller, and the photo-electric timer. These have been fully described elsewhere* and need no further comment.

Flash-welding of aluminium has met with no success but resistance butt welding is in considerable use, especially for wire. Improved results are said to be obtained by interposing a piece of aluminium foil, 0·3–0·4 mm. thick, between the ends to be butted. Current densities of the order of 50 amperes per square millimetre are required, and again, extremely accurate control is essential.

Hydrogen Penetration of Steel During Pickling.

THE presence of occluded hydrogen in sheet iron used for hot-dip galvanising results in the production of so-called " grey sheet " in the galvanising process. Some tests made by H. Bablik† indicate that the reason for the presence of undue amounts of occluded hydrogen is the accumulation of hydrogen sulphide in the pickling bath due to the reaction of the acid with the sulphide which is always present in commercial iron sheets. For a long time it has been noticed that the use of old pickling baths, especially those which " stink," leads to the formation of spots in the galvanised sheet, the spots being much more charged with occluded hydrogen than the remainder of the sheet. Britton, Hoar, and Evans,‡ in their work on the corrosion of iron in potassium chloride solutions, found that as little as 5 parts per million of hydrogen sulphide greatly accelerated corrosion, and attributed this behaviour to the formation of a non-protective film of iron sulphide instead of the usual protective film of corrosion product and the consequent enlargement of the reactive surface of the metal. Körber and Ploum‡ have also found that adsorption of hydrogen by cathodically polarised iron is greater in the presence of sulphides, selenides, and tellurides.

To obtain further information on the problem,

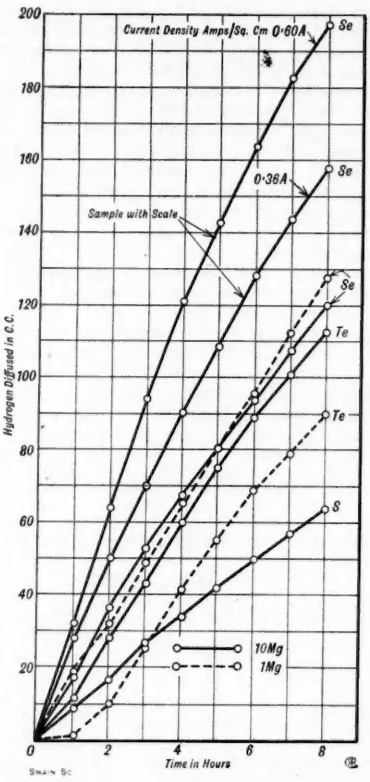

FIG. 1—*Relation between Hydrogen Diffusion and Time on Addition of Hydride-forming Elements of the VIth Group of the Periodic System.*

Bablik allowed iron sheets to be attacked by pickling acid on one side only, and measured the hydrogen evolved on that side and the hydrogen which diffused through the metal. In 9 per cent. pure hydrochloric acid the amount of hydrogen diffusing through the metal was about half that which diffused when 35 per cent. sulphuric acid was used; with commercial hydrochloric acid practically no diffusion occurred owing to the presence of arsenic, which removed the hydrogen sulphide immediately it was formed. Addition of soluble sulphides to the pickling acid increased the amount of diffused hydrogen proportionally to the square root of the concentration of the sulphide in the acid. Colloidal sulphur additions

* R. Salelles, *Rev. Soud. Autogène*, 1935, 27 (260), 2; J. W. Dawson, Iron and Steel Institute, Symposium on Welding, 1936, 2, 55.

† *Korrosion u. Metallschutz*, 1935, 11, 169.

‡ *J.* Iron and Steel Inst., 126, 335.

‡ *Mitt. K.-Wilh. Inst. Eisenforsch.*, 1932, 14, No. 16, 229.

produced a very large increase in the amount of diffused hydrogen, whereas additions of gelatine or mercury salts reduced the diffused hydrogen almost to zero. These results indicate that care should be taken to keep the sulphur content of pickling baths as low as possible to avoid adsorption of hydrogen by the metal and the consequent product of " grey sheets " in the galvanising process.

The more extended use of the Bullard-Dunn electrolytic pickling process, especially in America, has incited W. Baukloh and G. Zimmermann§ to study the mechanism of the adsorption of cathodic hydrogen by iron, since this adsorption can produce serious brittleness in the metal. The tests were made in an apparatus in which the cathode iron sheet

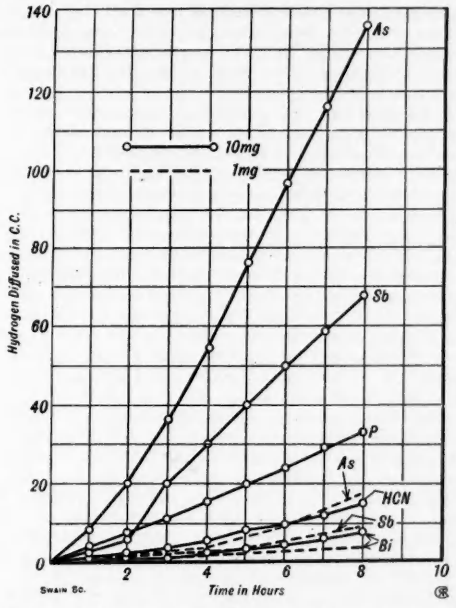

FIG. 2—*Relation between Hydrogen Diffusion and Time on Addition of Hydride-forming Elements of the Vth Group of the Periodic System.*

formed the bottom of the electrolytic vessel, and the volume of hydrogen diffusing through it was measured by means of a manometer. In 10 per cent. sulphuric acid the quantity of hydrogen diffusing through the metal decreases rapidly with increasing roughness of the sheet whether caused by a preceding pickle or by mechanical means. On the other hand, annealing in air, with or without a subsequent pickle in nitric acid, increases the amount of hydrogen diffusing through the metal owing to opening up of the grain boundaries. The amount of diffused hydrogen increases rapidly with increasing current density to a maximum at 3 amperes per square dm., then decreases at a slower rate with further increase in current density. Increase in the acid concentration increases the diffusion up to about 10 *N*-acid, then decreases it, the value for 20 *N*-acid being less than for 0·01 *N*-acid.

Elements which readily form hydrides, *i.e.*, the elements of the Groups V and VI of the periodic system, considerably increase the rate of diffusion of hydrogen as will be seen from Figs. 1 and 2. Selenium is by far the most active in this respect, and arsenic comes next; hydrogen sulphide is also an active promoter of diffusion as shown in Fig. 3. Mercury, lead, zinc, and cadmium have a much less marked action in promoting diffusion, while nickel, cobalt, copper, tin, and silver are quite inert.

Comparative tests made under the same conditions with and without additions of hydride-forming elements to the acid showed that copper, aluminium, magnesium, zinc, and nickel are quite impermeable to hydrogen in electrolytic pickling baths containing sulphuric acid.

In hydrochloric acid pickling baths the evolution

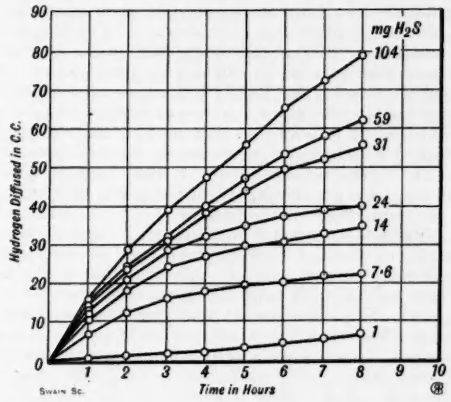

FIG. 3—*Effect of Additions of Hydrogen Sulphide to the Pickling Bath on the Hydrogen Diffusion.*

of chlorine at the anode has a strong depolarising effect on the hydrogen evolved at the cathode, and the amount of this gas which diffuses through the iron is therefore much smaller. Additions of selenides and tellurides to the bath considerably increase diffusion as in the sulphuric acid baths, but addition of arsenic has a much smaller effect and addition of hydrogen sulphide is without effect since it is immediately oxidised by the chlorine; electrolytic pickling in hydrochloric acid is therefore preferable to ordinary immersion pickling.

Electrolytic degreasing in alkaline baths does not produce brittleness by hydrogen absorption if the solution is pure; the presence of arsenic, however, results in considerable adsorption of hydrogen.

Arch. Eisenhüttenwesen, 1935–6, 9, 459.

Grinding and Polishing for Micrography.

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No. I.

THE amount of information published annually about the preparation of microsections for examination is surprisingly large; but, nevertheless, much of it is scattered through the literature in such a way that it is not always easy to locate. This is true more

particularly of etching reagents and methods, because they are often described in a few lines in the course of a report covering a much wider field. During the past few years, however, a number of papers have been published dealing specifically with methods of preparing specimens for microscopic examination. Some of these methods are intended purely for routine preparation of samples, but others are designed for more critical work and to avoid some of the troubles to which ordinary methods give rise. It is thought, therefore, that a short account of some of the recent work in this connection will be of interest. It is proposed to confine attention to grinding and polishing technique, but a few notes on mounting media are included at the end.

For ordinary routine work Pulsifer[1] has described a method of rapidly preparing for examination specimens of medium hard materials, such as bronze, brass, cupro-nickel, and mild steel. The idea is not to produce a proper metallographic polish on the surface, but merely to smooth it preparatory to chemical attack, the final elimination of scratches being left to the etching reagents employed. The method is as follows :—A flat surface having been obtained by filing, the specimen is rubbed down by hand to " 000 " emery paper. If the specimen is an iron or steel it is now slightly etched before proceeding to the next stages of the process, which are intended to eliminate the usual method of polishing on a rotating cloth disc. These stages consist of smoothing operations carried out by rubbing the specimen lightly on flattened heaps of damp abrasive placed on cloth or chamois leather stretched over paraffined boards. Two such boards are used with carborundum powder (" No. 600 grit ") on one and ground tripoli on the other, both abrasives being well washed before use. Each heap is moistened just enough to hold together and to support the specimen as it is rubbed very lightly on the abrasive. The specimen should not be allowed to come into contact with the underlying cloth. A sequence of light etching and then a few seconds rubbing repeated about three times on each abrasive is stated to leave the specimen in a condition satisfactory for etching. The surface is not polished, but has a granular or matt appearance, and the final etching necessary to reveal the structure reasonably clearly is apparently rather deep. Pulsifer's method, therefore, while useful for rapid examination of structures at low magnification, seems to be unsuitable for work involving high resolving power. Nevertheless, the method provides a means of quickly preparing microsections entirely by hand, as, of course, grinding wheels and fabrics on rotating discs are not used. It is apparently possible, after some practice, to grind smooth and etch a specimen in five minutes or less.

The greatly increased attention now being paid to the study of non-metallic inclusions in metals has led to the introduction of methods of grinding and polishing designed, firstly, to prevent such inclusions from falling out of the surface being prepared for examination and, secondly, to preserve their natural colours and characteristics, thus enabling them to be identified with greater certainty. Evidence is accumulating that, with these objects in view, dry grinding and dry, or practically dry, polishing should be exclusively employed, and that, as far as possible, liquids should not be allowed to come into contact at any stage with the surface being prepared. When liquids are used in these operations there is apparently the possibility that they will penetrate into the boundaries between the inclusions and the metal, thus loosening the former. It is to be expected that there will be more tendency for this effect to occur the greater the wetting power of the liquid used and the lower its viscosity ; but, nevertheless, even with highly viscous lubricants, such as oil or vaseline, there is still some risk of loosening the inclusions.

Benedicks and Wretblad, whose work is referred to later, think that probably the fundamental reason for the great tendency of slag particles to work out of the surface being prepared is that the inclusions and the metal have different thermal coefficients of expansion. If, as is usually the case, the metal on cooling contracts more than the slag, it is clear that inclusions of the latter will be subjected to very considerable pressure, and this may then cause them to be squeezed out of the metal whenever they are brought to the surface during grinding. If, on the other hand, the metal contracts less than the slag, it follows that the pressure on the latter may decrease to such an extent that the particles become quite loose and thus easily drop out during the grinding of the surface.

A method of dry polishing which will retain graphite and inclusions in cast irons and steels has been described by Urban and Schneidewind.[2] There are four stages as follows :—(*a*) Light grinding on fine wheel ; (*b*) grinding on leather wheel charged with a mixture of alumina and pumice cast in stearic acid ; (*c*) polishing on leather wheel, or on disc covered with billiard cloth with alumina cast in stearic acid ; if the disc is used water is dropped on very sparingly ; (*d*) final polishing on disc covered with billiard cloth charged with jewellers' rouge cast in stearic acid. The leather wheel used in stages (*b*) and (*c*) is of the type used by electroplaters and is 20 cm. in diameter, faced with sheepskin, and rotates at 1750 r.p.m. The principle of the method is to avoid loose powder abrasives and water as much as possible.

Priestley[3] has also described the use of a rouge and stearic acid mixture for dry polishing cast iron specimens which have been rubbed down to " 000 " paper in the usual way. The polishing mixture is used on a medium-nap cloth disc rotating at 400 to 600 r.p.m., and only a little water is employed as a lubricant for the specimen. Priestley notes that the graphite flakes and inclusions in cast iron are still intact when the specimen leaves the " 000 " paper, but are badly eroded if the final polishing is then carried out on cloth with alumina and water—that is, with a loose polishing medium. It appears that this latter condition is not desirable if good results are to be obtained, and by showing that this erosion does not occur with the rouge-stearic acid mixture he implicitly confirms the principle adopted by Urban and Schneidewend, as mentioned above.

Vilella[4] recommends the following technique for retaining graphite in cast iron. Grind at moderate speed on emery papers down to " 000," being very careful to avoid scratches on the latter. Now take the same sheet of " 000 " paper, glaze it by rubbing it with graphite or soapstone, and use it for fina grinding, being careful to use light pressure. Polishing is then carried out with levigated alumina or heavy magnesia on the dull side of heavy pure silk satin. The polishing powder should be applied dry to the wet cloth and rubbed in with the fingers, all gritty particles being worked out. Epstein[5] considers that the use of costly satin is an unnecessary refinement because excellent results can be obtained with cheap velveteen cloth.

The properties of the supporting medium for the abrasive are of considerable importance, particularly

when photomicrographs are to be taken at the highest magnifications, because such work calls for specimens with surfaces everywhere perfectly flat. When using cloth or paper as the support for the abrasive the edges of the specimen always become rounded and the actual surface becomes slightly convex. This is due to the elastic flexure of the support. Furthermore, polishing on elastic material, such as wet felt, generally makes the harder constituents of the specimen stand in relief. This effect is, of course, the basis of the well-known method of "relief polishing" devised by Osmond. Hence, to obtain a surface which is truly plane it seems rational to employ a rigid and inelastic support for the abrasive. While relatively inelastic supporting media, such as paraffin wax, have been used by Dowdell and Wahll and others, following Gutrie[6], investigations have been carried out by Benedicks and Wretblad involving the use of discs of lead.

Dowdell and Wahll[7] use the following method. After grinding down to "0" paper, finer grinding is carried out, without using water, on vertical discs 20 cm. diameter upon which a molten mixture of paraffin wax and abrasive has been allowed to solidify. Two discs are used, and the abrasives are 150 mesh and 400 mesh carborundum respectively. The wax is melted and then sufficient abrasive added to form a thick mud, which, after well stirring, is cast into the mould formed by fixing a suitable metal band round the edge of the disc. The abrasive settles rapidly, and so, when the mixture is solid, a layer of nearly pure wax is left on top. This is removed with a straight edge tool, and the discs are then ready. With proper use they should last several months. It is stated that almost any grade of abrasive may be employed in this way, and that no tendency has been observed for the wax to work loose from the underlying disc. The advantages claimed for this method over emery papers are: (1) The abrasive is not worked into the surface of soft metals, (2) it is extremely economical, (3) specimens do not get hot or "flow" excessively when heavy pressure is used, and (4) it is very rapid, aluminium, magnesium, copper, and steel being polished in one-third of the usual time.

As part of a comprehensive series of researches on non-metallic inclusions in steel Benedicks and Wretblad[8] have carried out a detailed investigation concerning the preparation of plane surfaces by dry grinding and dry polishing, and have worked out a method for dry grinding with abrasive powder on lead discs rotating at 400 to 900 r.p.m. The surface of each disc is provided with a system of two parallel grooves cut in the form of spirals of Archimedes. The pitch is about 12 mm. and the distance apart of the two grooves is maintained at half the pitch. The grooves are 0·5 mm. wide and 0·5 mm. deep, and are carefully rounded at the bottom. Their chief function is to take up the excess of grinding medium, and their spiral form makes the cleaning of the disc much easier than would be the case with, for example, a system of grooves crossing in various directions. By using these discs with ordinary commercial abrasive powders, and with specially prepared grades of very uniform grain size (see below), specimens of iron and steel can be rapidly provided with perfectly flat, finely ground, surfaces suitable for immediate polishing in the normal way on wet cloth where ordinary microscopic work is concerned. For dry polishing to preserve inclusions the use of such discs and the finest grade of abrasive is not entirely satisfactory, although a surface which might be termed polished can be obtained. The difficulties here are caused by the loose polishing powder, and it has been found an advantage to use, instead of a lead disc, one of glass coated with cellulose lacquer. The glass disc is prepared for use either by spraying with a suspension of the polishing medium in dilute lacquer, or by the following method, which gives a more level surface. A quantity of dilute lacquer (6 c.c. for an 18 cm. disc) is poured over the horizontal disc in a dust-free room and then allowed to dry for twenty-four hours in an atmosphere of the lacquer solvent. The lacquer is now covered with polishing powder, which is worked into the surface with a soft brush, and the excess removed. The powder remaining on the surface is cemented to it by spraying with a small quantity of the lacquer solvent and the disc then set aside to dry for half an hour. The process of working polishing powder into the surface, spraying with solvent and drying is repeated about six times. After a final drying for twenty-four hours the disc is ready. To prevent seizing between specimen and disc when in use some washed graphite is put loosely on the latter three or four times per hour. Polishing under these conditions is very slow, and an hour or two is required for each grade of polishing material used. (It should be remembered that the ultimate object of this method of polishing is to enable inclusions to be photographed at high magnifications of 1200× or more.) Benedicks and Wretblad have therefore constructed and described a suitable automatic polishing machine for the work. One of the troubles associated with dry polishing is the formation of a thin oxide film on the surface of the specimen. It has been found that this can be avoided by continuously removing the loose grinding dust with an adhesive roller, or by polishing in a nitrogen atmosphere.

It may be mentioned here that Portevin and Castro[9] are of the opinion that it is not necessary to use any special "dry polishing" technique in the study of inclusions. They employ ordinary methods involving coarse grinding on a wheel or emery paper, followed by polishing with two grades of alumina, taking care that (*a*) only worn emery paper is used, (*b*) the specimen is not pressed too heavily on the abrasive, and (*c*) the specimens are finished off for a sufficient length of time with almost dry felt.

In the second part of this paper, which will appear in the October issue, improvements in the preparation of graded abrasives and polishing powders are discussed and methods of mounting specimens are considered.

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(*To be continued.*)

Surface Hardening of Manganese Steel.

THE notable resistance to wear offered by manganese steel is only evident after a certain amount of deformation has taken place. When high pressures are not involved the full resistance to wear is not developed, and in such circumstances manganese steel cannot usefully be employed; neither can it be used if it is essential that the original dimensions of the component should be strictly preserved. A desire to extend the use of manganese steel to meet such conditions has given rise in the research department of the Skoda Works to investigations which are described by E. Valenta and V. Koselev* under the title "The New Processes of Surface Hardening of Austenitic Steels."

It is well known that the austenitic character of manganese steel depends on its composition and rate of cooling. A series of compositions forming a limit of the purely austenitic steels may be determined for any rate of cooling. With a given manganese content, the boundary of the austenite region may be crossed if the carbon is reduced. With the same treatment the material is then martensitic and the higher the manganese the lower will be the carbon content required to produce martensite. For example, with 11 per cent. of manganese the carbon has to be reduced to 0·3 per cent. to obtain the first traces of martensite in the quenched steel, but with 8 per cent. of manganese martensite appears with 0·7 per cent. carbon, and the steel is wholly martensitic when the carbon is reduced to below 0·3 per cent.

The suggested process of surface hardening is therefore to decarburise manganese steel of suitable composition by prolonged heating in air before the final quenching operation. While the Vickers diamond hardness of the austenitic core is about 250, that of the decarburised region reaches a value of 550 to 600, though there is the disadvantage that the maximum hardness is only reached at some distance below the surface, and that for about 1 mm. from the outside the hardness is gradually rising from the very low figure resulting from over-decarburisation. The authors' remedy for this is either to grind off the low-carbon surface before use, or to recarburise the outer layer before the final quenching treatment.

Valenta and Koselev hold that when this process is adopted it is unnecessary to use steel with such a high manganese content as in Hadfield's manganese steel, but that steels with 7 to 9 per cent. of manganese are more suitable.

While it may be admitted that all the structural changes and mechanical properties claimed by the authors will readily be obtained in the manner described, the question still remains whether the martensitic layer so produced will have the exceptional wear-resisting quality of the altered layer of the original austenitic steel. In other words, will the resistance to wear be that of the hardened layer mechanically produced on the austenite or only that of a partially carburised surface on a case-hardening steel. This question, of course, can only be answered by experience, but it seems likely that it is not merely the martensitic structure produced by deformation of the surface layers, but the carbon content and texture of the martensite that contribute to the wear resistance on which much of the utility of manganese steel is based.

* *Revue de Métallurgie*, July, 1936, Vol. 33, pages 466–472.

Undisturbed Solidification.

THE concavity of surface of a metal solidifying in an open mould and the phenomenon of piping are dependent on the action of shrinkage coupled with that of gravity. Blow-holes, which counteract piping, result from the entrapment of gas liberated during solidification. Whether the gas escapes or not is largely determined by the nature of the temperature gradient set up in the solidifying metal by the cooling action of the mould and the surrounding air.

In a recent investigation A. Glazunov and N. Lazarev* have endeavoured as far as possible to eliminate the effects of both gravity and temperature gradient during solidification. To achieve this they have imitated, with metal and at a high temperature, the well-known experiment in which a large globule of oil is held in suspension in an alcohol-water mixture or one of aniline is made to rise and fall in water by a change in temperature influencing their relative densities. Light metals only could be used, as it was necessary to find a liquid medium of specific gravity equal to that of the liquid metal at the temperature of solidification. It was also essential that no chemical reaction should take place between the metal and the bath.

For magnesium a mixture of 85 per cent. of lithium chloride and 15 per cent. of lithium fluoride was found suitable. Its specific gravity at 650 deg. Cent. was 1·6. A globule of 20 to 30 grammes of magnesium would remain suspended in the salt, which was very slowly cooled through the freezing point of the metal. The solid magnesium was then withdrawn and cooled in water. Its form was that of a perfectly regular sphere, except that its surface showed the outlines of polyhedral grains of large dimensions. The microstructure of a section was uniform and showed that crystallisation had begun almost simultaneously at the surface and in the interior. The contraction also had been perfectly uniform, and there was no sign of a cavity.

Aluminium was studied in the same way and with similar results. The medium found suitable for the suspension of aluminium globules contained barium chloride 40 per cent., calcium chloride 45 per cent., and sodium chloride 15 per cent.

The authors conclude that metals protected from the influence of gravitation and from the chilling effect of a mould wall during freezing solidify into a compact mass and show neither cavities nor blow-holes.

Though further work might be done on aluminium alloys, it is unfortunate that there does not seem to be any possibility of extending this very interesting form of experiment to the alloys of such metals as copper or iron, on account of their high densities.

* "The Crystallisation of Metals Without the Influence of Gravitation," *Revue de Métallurgie*, July, 1936, Vol. 33, pp. 438–441.